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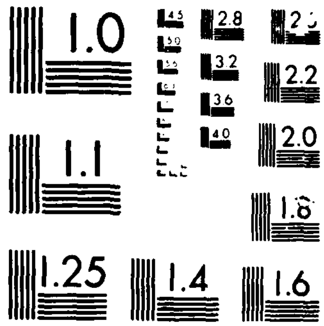
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PREPARATION AND CHARACTERIZATION OF MEMBERS OF THE CHROMIUM-ZIRCONIUM OXIDE SYSTEM

by

Ping Wu, Robert Kershaw, Kirby Dwight, Aaron Wold

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Brown University
Chemistry Department
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1. Abstract

Samples of zirconium oxide containing 5-20 atomic percent chromium were prepared by double decomposition of the nitrates. X-ray diffraction analysis showed the products to be single phase. Magnetic susceptibility measurements were used to characterize the formal oxidation state of the chromium.

2. Introduction

Magnetic studies of the chromium-aluminum oxide system were reported by Eischens and Selwood (1) and indicate that the average valence of chromium is dependent upon the method of sample preparation. Matsunaga (2) has reported that the high average oxidation state of the supported chromium oxide on alumina is due to surface oxidation.

It has been shown t' ^ stabilized cubic ZrO_2 containing chromium can be prepared (3, 4). Walter et al. (5) measured the magnetic properties of the catalyst system ZrO_2-Cr_2O_3 and demonstrated the existence of Cr(IV), Cr(V) and Cr(VI) in addition to Cr(III). However, there has been no detailed study showing the relationship between the magnetic properties and the structure of members of the chromium-zirconium oxide system as a function of chromium content. It is therefore the purpose of this study to investigate these relationships.

3. Experimental

Bulk chromium (III) oxide samples containing varying quantities of chromium (IV) oxide were prepared by decomposition of $Cr(NO_3)_3 \cdot 9H_2O$. The nitrate was dissolved in water and dried at 150°C for 12 hours. The samples were then ground and decomposed at temperatures ranging from 450°C to 800°C. The final products contained varying amounts of Cr(IV). Zirconium oxide samples containing various percentages of chromium were prepared by mixing the desired quantity of analyzed chromium nitrate $Cr(NO_3)_3 \cdot 9H_2O$ with appropriate amounts of $ZrO(NO_3)_2$. The atomic percent of chromium reported in this study corresponds to the ratio Cr/(Cr+Zr). Two ml of water was added for each millimole of total nitrates. The solution was then dried at 150°C for 12 hours and the product was ground and heated at 600°C for 24 hours. Some samples were then subsequently heated at elevated temperatures between 650-1100°C for 24 hours. In order to ensure that all of the chromium was chromium (III), a portion of the 20at% sample was heated at 600°C and then reduced in a 85%Ar/15%H_2 atmosphere at 600°C for 8 hours. In order to ascertain the appropriate temperature of complete decomposition of the nitrate, preliminary decomposition experiments were carried out in a Cahn System 113 thermal balance.

A sample of 10 mole percent chromium oxide supported on ZrO_2 was also prepared by the incipient wetness method. $ZrO(NO_3)_2$ was dissolved in water and dried at 150°C for 24 hours and then heated at 400°C for 24 hours. A calculated quantity of $Cr(NO_3)_3 \cdot 9H_2O$ was dissolved in water and the appropriate weight of ZrO_2 was dispersed into this solution and stirred for about ten minutes. The resulting impregnated ZrO_2 was dried at 150°C for 12 hours and the product was ground and heated at 600°C for 24 hours. For the preparation of this sample, 20 ml of 0.1M $Cr(NO_3)_3 \cdot 9H_2O$ was used for each gram of ZrO_2.

X-ray powder diffraction patterns of the samples were obtained using a Philips diffractometer and monochromated high intensity $CuK\alpha_1$ radiation (λ = 1.5405Å). The diffraction patterns were taken in the range $12° < 2\theta < 80°$ with a scan rate of 1° 2θ min^{-1} and a chart speed of 30 in h^{-1}.

Magnetic susceptibilities were measured using a Faraday balance at a field strength of 10.4 kOe. Honda-Owens (field dependency) plots were also made and all magnetic susceptibility data were corrected for core diamagnetism. Magnetic susceptibility measurements were made from liquid nitrogen temperature to 315K.

4. Results and Discussion

Bulk samples of chromium (III) oxide were prepared by the decomposition of $Cr(NO_3)_3 \cdot 9H_2O$. When the nitrate was heated at 450°C for one hour, the product appeared black and x-ray diffraction analysis (Fig. 1) showed the presence of CrO_2. After further heating at 450°C, for a total of 24 hours, the diffraction pattern of the product showed the presence of a single phase which corresponded to Cr_2O_3. However, the dependence of susceptibility upon field shown in Fig. 2 indicated that a small ferromagnetic phase was still present, which was probably due to remaining traces of CrO_2. When the oxide was heated to 800°C for 24 hours, the resulting product appeared green and gave no evidence either by x-ray analysis or field dependency measurements (Figs. 1, 2) for the existence of CrO_2 in the product.

Samples of the ZrO_2-Cr_2O_3 system were prepared by the double decomposition of $ZrO(NO_3)_3 \cdot 9H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$. Whereas decomposition of zirconyl nitrate proceeded completely below 500°C and the final product was tetragonal ZrO_2 (6), the decomposition of the double chromium-zirconium nitrate required a temperature of 600°C in order for complete conversion to the oxide. X-ray analyses of products containing varying atomic percent of chromium are given in Table I. The representation of the chromium loading in Table I was chosen because the oxidation state of chromium varies from sample to sample.

Decomposition of pure zirconyl nitrate, in the absence of chromium, at 600°C results in the formation of tetragonal ZrO_2 containing a small quantity of monoclinic ZrO_2. For the samples prepared by double decomposition of the nitrate, x-ray diffraction analysis indicates the absence of any chromium oxide.

However, the structure of the zirconium oxide underwent a gradual transformation from tetragonal to cubic, indicating that chromium was stabilized within the fluorite structure. Stabilization of the cubic form of ZrO_2 requires the presence of a solid solution with the chromium oxide. This was demonstrated by Stöcker and Collongues (3).

TABLE I

Composition	Phases obtained after decomposition of nitrate at 600°C
ZrO_2	Tetragonal ZrO_2 + small amount monoclinic ZrO_2
Cr/(Cr+Zr) = 5%	Tetragonal ZrO_2 + trace monoclinic ZrO_2
Cr/(Cr+Zr) = 10%	Tetragonal ZrO_2
Cr/(Cr+Zr) = 15%	Pseudo cubic ZrO_2
Cr/(Cr+Zr) = 20%	Cubic ZrO_2

In order to ascertain the oxidation state and nature of the chromium associated with the ZrO_2, magnetic measurements were made as functions of both field and temperature. Whereas bulk Cr_2O_3, prepared below 800°C, showed a field dependency indicative of the presence of CrO_2 contamination, none of the zirconium oxide samples containing chromium showed any such field dependency. This indicated that bulk CrO_2 was not present in any of the products prepared at 600°C. It had been shown that this temperature was necessary for the complete decomposition of the mixed nitrate to the oxides.

The paramagnetic moments of the 5-20 atomic percent loading of chromium are given in Table II. From the moments found for the various samples of ZrO_2 containing chromium, it can be seen that most of the chromium is present as Cr(IV). There also appears to be an increase in the observed moment with increasing chromium loading. This is consistent with the possible existence of Cr(V) $3d^1$ in the sample and agrees with the results of Matsunaga concerning chromium oxide supported on aluminum oxide. In order to confirm the existence of Cr(IV) in ZrO_2, a sample of 20at% Cr/(Cr+Zr) was heated in a stream of

TABLE II

Loading (at% Cr/Cr+Zr)	Temperature of preparation	Paramagnetic moment $P_{expt'l}$
5	600	2.50
10	600	2.64
15	600	2.81
20	600	2.92

*Moment per Cr; Spin only moment for Cr(IV) 2.83, for Cr(III) 3.87.

85%Ar/15%H_2 at 600°C for 8 hours. The results of the magnetic measurements are indicated in Fig. 3. From this data the paramagnetic moment was calculated to be 3.65 B.M., which corresponded closely to the conversion of Cr(IV) to Cr(III) within the cubic ZrO_2 structure. X-ray analysis of the reduced sample indicates no appreciable change in the structure of the ZrO_2 sample containing Cr(III). ZrO_2 samples containing up to 20 atomic percent chromium remain stable until approximately 700°C; above this temperature Cr_2O_3 begins to appear in x-ray diffraction patterns of the products and the ZrO_2 gradually transforms to the monoclinic form.

Another sample of ZrO_2 containing 20at% Cr was prepared by incipient wetness. A 0.5M solution of chromium nitrate was added to tetragonal ZrO_2 and decomposed at 600°C. X-ray diffraction analysis indicated that both Cr_2O_3 and the starting ZrO_2 were the only phases formed. There was no evidence for the formation of a solid solution between chromium and zirconium oxides.

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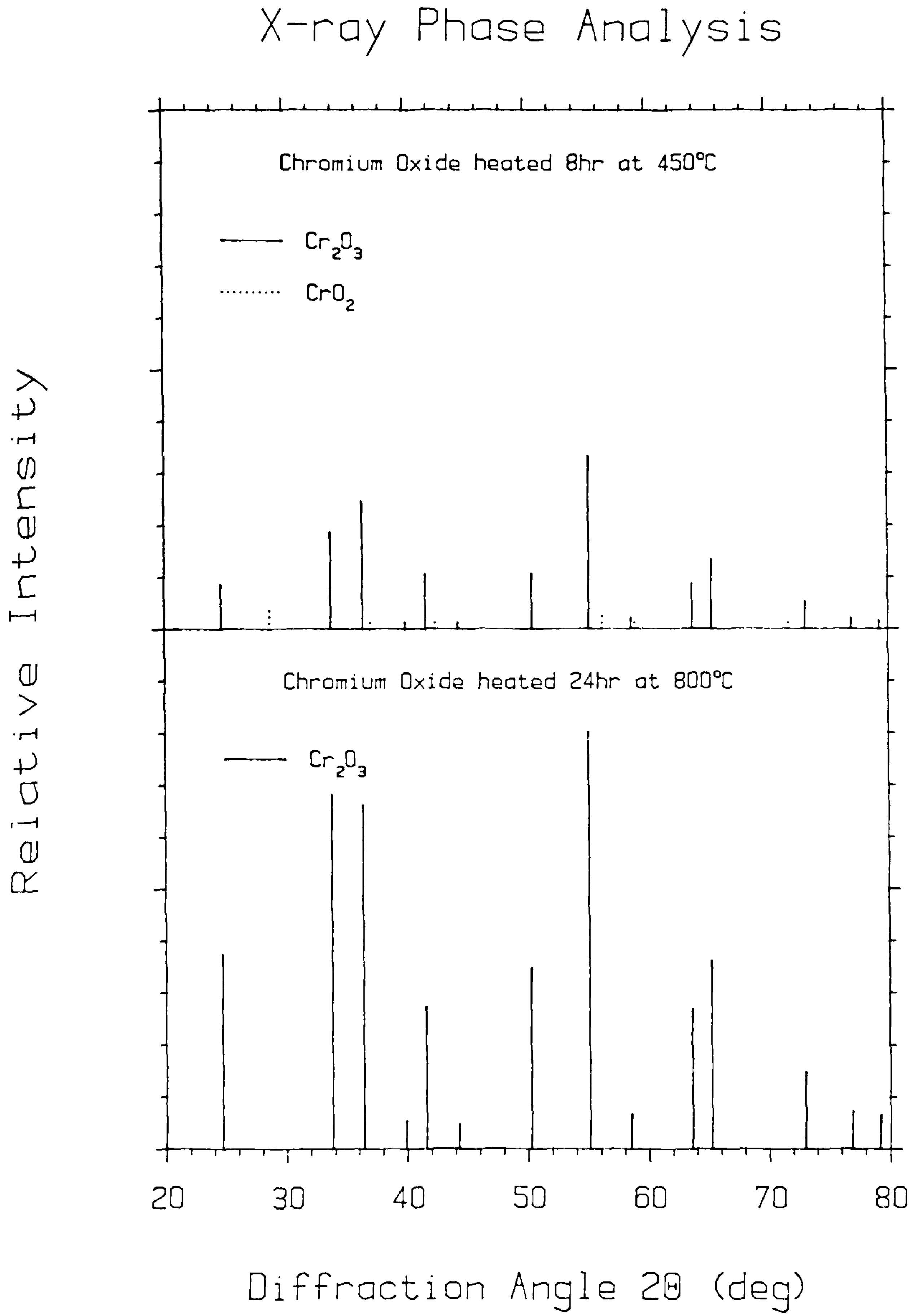
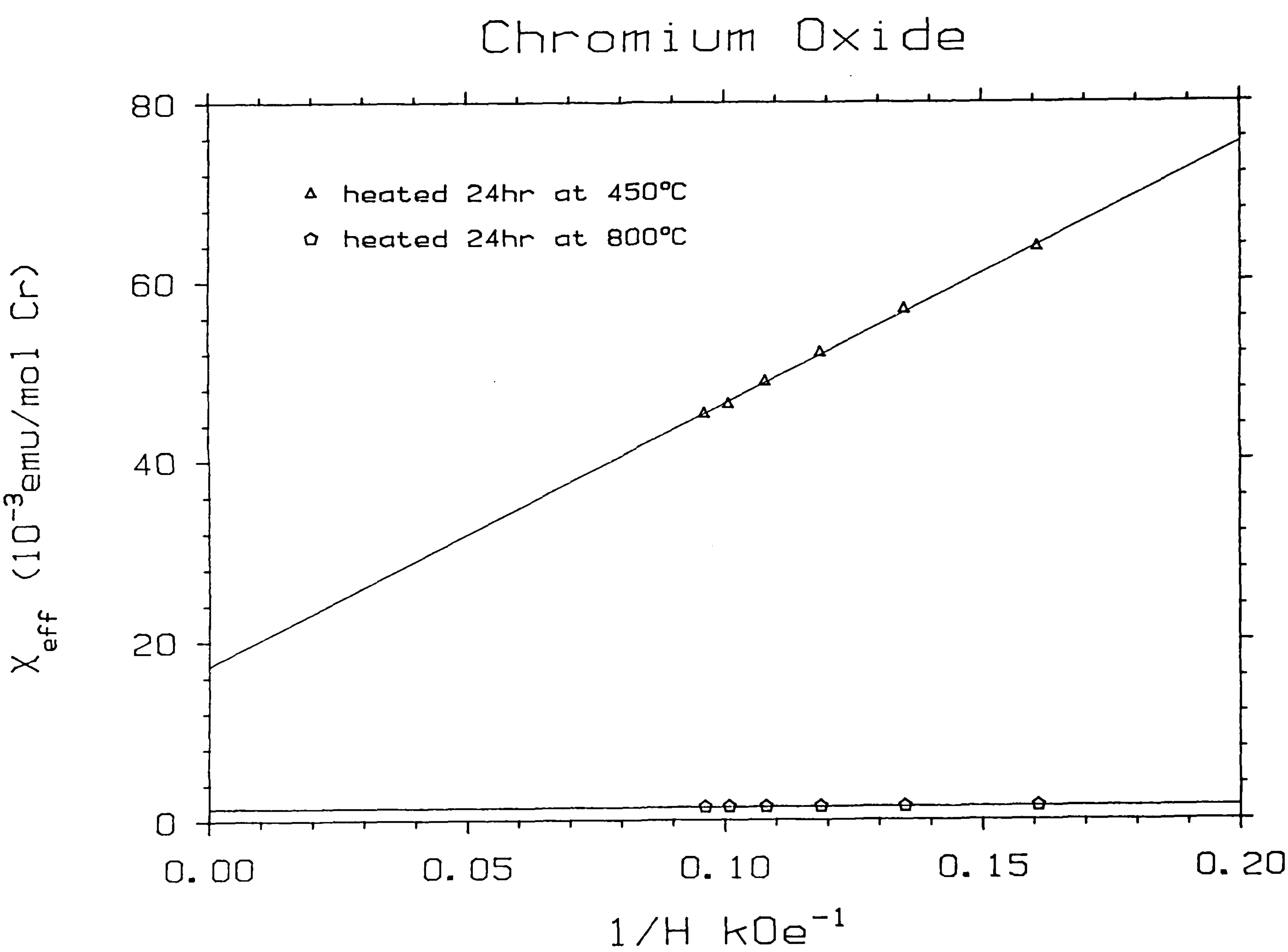
FIGURE CAPTIONS

Fig. 1. X-ray phase analysis of chromium oxides prepared at 450°C and at 800°C

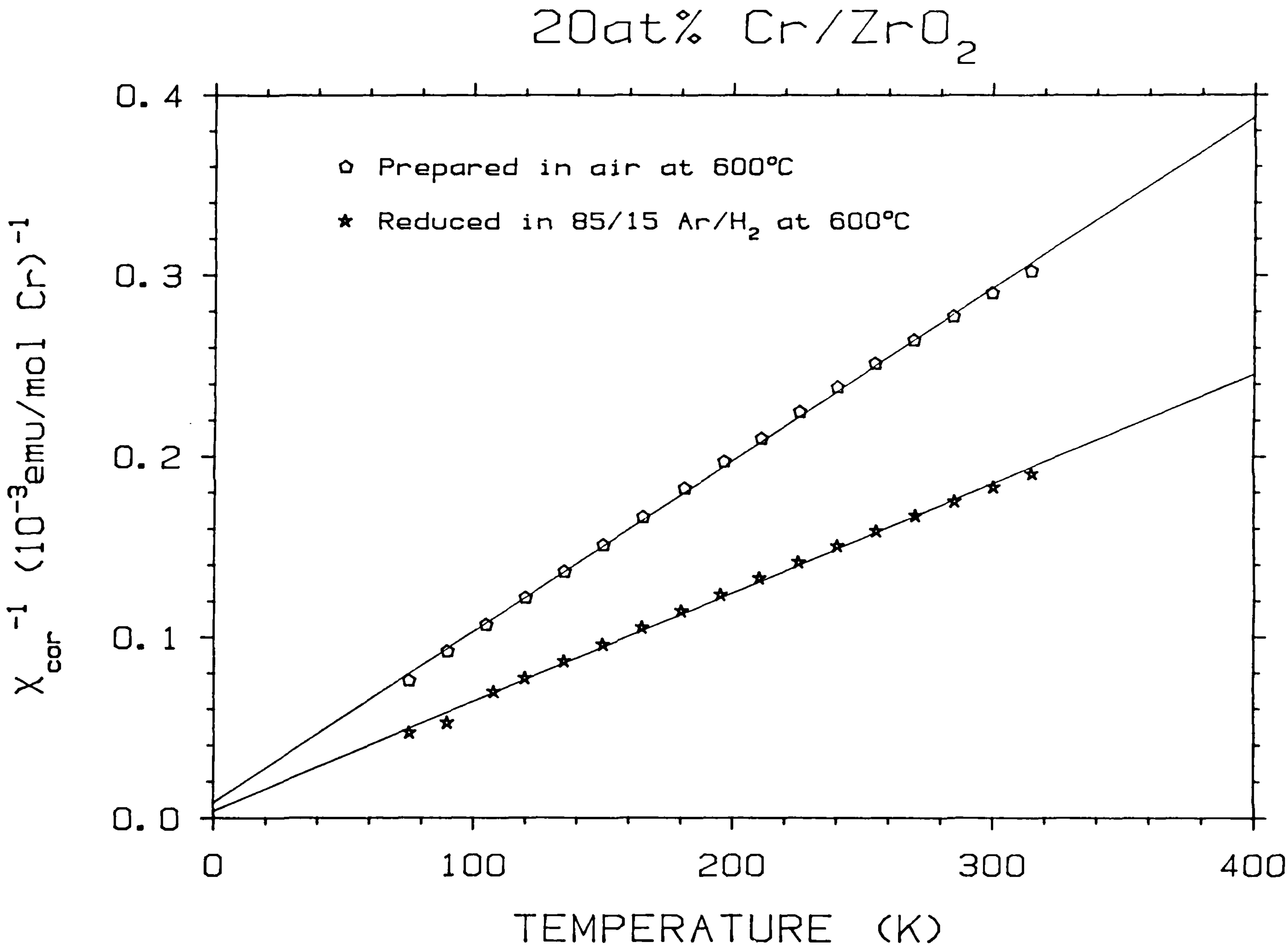
Fig. 2. Dependence of effective magnetic susceptibility upon inverse applied field at 77°K for chromium oxides prepared at 450°C and 800°C.

Fig. 3. Temperature dependence of the corrected magnetic susceptibility per mol of Cr of 20 atomic percent Cr/ZrO_2 samples both prepared in air at 600°C and reduced in 85/15 Ar/H_2 at 600°C.


X-ray Phase Analysis
Chromium Oxide heated 8hr at 450°C
Cr2O3
CrO2
Chromium Oxide heated 24hr at 800°C
Cr2O3
Relative Intensity
20
30
40
50
60
70
80
Diffraction Angle 2Θ (deg)



Chromium Oxide
heated 24hr at 450°C
heated 24hr at 800°C
80
60
40
20
0
0.00
0.05
0.10
0.15
0.20
χ_{eff} (10^{-3}emu/mol Cr)
1/H kOe^{-1}


20at% Cr/ZrO2
Prepared in air at 600°C
Reduced in 85/15 Ar/H2 at 600°C
χcor^-1 (10^-3emu/mol Cr)^-1
0.0
0.1
0.2
0.3
0.4
0
100
200
300
400
TEMPERATURE (K)

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